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Palladium(II) Complexes of N,N-Dimethyl-cinnamylamine

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Abstract

At-20°C, lithium chloropalladite(II) reacts with N,N-dimethylcinnamylamine in methanol to give π-complex, dichloro-(N,N-dimethylcinnamylamine)-palladium(II) (**2**), in 84% yield. By stirring in methanol at room temperature the π-complex(**2**) convert to σ-complex, di-μ-chloro-bis-(1-phenyl-2-methoxy-3-N,N-dimethylaminopropyl)-dipalladium(II) (**3**), in 88% yield. NMR spectrum study on the σ-complex(**3**) shows that the *trans* addition of methoxy group to the co-ordinated olefin occurs.

Introduction

The addition of nucleophiles to the carbon-carbon double bond of olefin-palladium and -platinum complexes has received wide attraction.[1] The suggestion[2] that the mechanism of the Wacker oxidation of olefins involved *cis* stereochemistry in the rate-determining hydroxypalladation step has been generally accepted and assumed to applly to all the similar reactions in which nucleophilic attack on olefins co-ordinated to palladium(II) and platinum(II) take place. The *cis* hydroxypalladation mechanistic suggestion was based primarily on kinetic results, but the data are also consistent with *trans* stereochemistry for the addition. Thus, the stereochemical path of the methoxypalladation and methoxyplatination of chelating diolefins, which was demonstrated to take place *trans* in every case,[3] was regarded as anomalous.

In order to explain this assumed anomaly, it was suggested that the reaction of the bicyclic chelating diolefins followed the *trans* stereochemical path for steric reasons.[4~6] The *trans* stereochemistry has also been attributed either to the inability of the chelating diolefins to rotate 90° from the position perpendicular to the square plane of the metal complex into a position which would favor *cis* addition by metal and a ligand attached to it,[7] or to the fact that methanol does not co-ordinate to the metal prior to addition.[8] There is

increasing evidence, however, that when a nucleophile such as acetate,[9] chloride,[10] or amine[11] is not co-ordinated to palladium prior to attack, the addition stereochemistry is *trans*, even with simple monoolefins.[12]

In the course of a study designed to explore the synthetic utility of palladium(II) catalyst, the reaction of N,N-dimethylcinnamylamine(**1**) with lithium chloropalladite in methanol was carried out.

Results and Discussion

Stirring solutions of **1** and lithium chloropalladite(II) in methanol at −20°C yielded a yellow crystal(**2**) which is stable at low temperature (<0°C), but decomposes slowly at room temperature to give a palladium mirror. The monomeric structure for **2** was supported by the molecular-weight determination. The IR spectrum of **2** showed a co-ordinated olefinic streching absorption at 1422cm^{-1}, and the far-infrared spectrum showed an absorption band at 350cm^{-1} which can be assigned to the terminal Pd-Cl streching. Morever, the π-complex structure for 2 was established by the NMR spectrum. The NMR spectrum of **2** consists of five resonances at σ 2.55, 3.38, 6.63, 6.98, and 7.25 *ppm* with relative intensities of 6:2:1:1:5. The singlet peak at σ 2.55 *ppm* and the doublet peak at σ 3.38 *ppm* can be assigned to, respectively, the N-methyl and N-methylene protons on the basis of the integral ratio and the chemical shifts. The doublet peak at σ 6.53 *ppm* (J=16Hz) and the triple-doublet at σ 6.98 *ppm* also can be assigned to the *trans*-olefinic proton, and the signal at σ 7.25 *ppm* corresponds to the phenyl protons.

When a suspension of **2** in methanol allowed to stir at room temperature, a yellow new complex (**3**) was obtained in good yields. It was also found that **1** reacts with lithium chloropalladite(II) in methanol at room temperature to give a same complex (**3**) in 64% yield. The σ-bonded structure for **3** was supported by the following data. The chloro-bridged binuclear structure was established by the molecular-weight determination and by the reaction with pyridine to give a readily soluble monomeric derivative (**4**). Furthermore, the infrared spectrum of **3** shows a bridged Pd-Cl streching absorption at 310 and 260cm^{-1}. The NMR spectrum of **3** is in agreement with the proposed structure. The singlet peaks at 2.60 and 2.78 *ppm* in this spectrum are assigned to the N-methyl groups, whereas the double-doublet peak (centered at *2.69* ppm), which overlape with two N-methyl peaks, are assigned to N-methylene protons (H_c and H_d) on the basis of the chemical shifts and the relative intensities. The nonequivalence of these N-methyl and N-methylene protons is most easily explained in terms of a cyclic system in which nitrogen is co-ordinated to the palladium metal and a palladium-carbon σ-bond exist. On the other hand, the sharp singlet peak at 3.07 *ppm* is assigned to the

methoxy protons. The doublet peak at 3.66 *ppm* (J=8.0 Hz) is assigned to the proton (H_a) on the carbon atom which is substituted by the phenyl group, and the multiplet peak (centered at 3.89*ppm*) is also assigned to the proton (H_b) on the carbon atom which is substituted by the methoxy group.

On the basis of the theoritical calculation of Karplus,[13] the value of coupling constant (J=8.0 Hz) between H_a and H_b indicates the resonable dihedral angles of C-H bond of about 160° and 8°. In the five membered rings, however, large coupling constant is ascribable to the "diaxial" hydrogen pair (*trans*), rather than the "equatirial-axial" pair (*cis*).[14] Now this σ-complex most likely exist in the conformation shown in **3**. However, this argument is some what termous, because coupling constants depend on the hybridisation of carbon as well as on the dihedral angle; and the hybridisation of the carbon to which the palladium is attached is uncertain. Previously, it has been shown that the reaction of nucleophile such as alkoxide ion,[3,6] β-diketone,[15,16] diethyl malonate,[16,17] and amines[11,17] with a cyclic diolefin complex such as dichloronorbornadiene palladium(II) (**5**) involves attack by the nucleophile on the olefinic group from the side opposite to the metal, this is, a *trans* addition takes place. Even with simple monoolefin complex, moreover, methoxypalladation proceeds *via trans* addition stereochemistry[12,18].

These result supports that, in the treatment of **2** with methanol, the reaction with methoxide anion proceeds by attack at the double bond on the side opposite from that which faces the palladium, and that consequently the structure of σ-complex must be **3**.

On the other hand, π-complex **2** reacts with ethanol at room temperature to give σ-complex (**6**). The infrared spectrum shows a dimeric bridged Pd-Cl streching absorption at 310 and 260cm^{-1}. The NMR spectrum of **6** is in agreement with the proposed structure. The triplet at 0.87 *ppm* and the quartet at 3.15 *ppm* correspond to the ethoxy protons, and the peaks at 2.64 and 2.76 *ppm* assigned to the N-methyl groups. Whereas, the peak (centered at 2.69 *ppm*) which overlape with the N-methyl groups, is assigned to the N-methylene protons on the basis of the chemical shift and the relative intensities. The nonequivalence of the N-methyl groups is explained in terms of a cyclic system, as well as in the case of **3**. Furthermore, the doublet peak at 3.60 *ppm* (J=8.0 Hz) is assigned to the methine proton (H_a) and the multiplet peak at 3.93 *ppm* is also assigned to the proton (H_b) on the carbon atom which is substituted by the ethoxy group. The value of coupling constant (8.0 Hz) between H_a and H_b would be expected in the diaxial hydrogen pair conformation (*trans*), rather than in the axial-equatorial (*cis*), and then these results support the proposed structure **6** for the ethoxy complex.

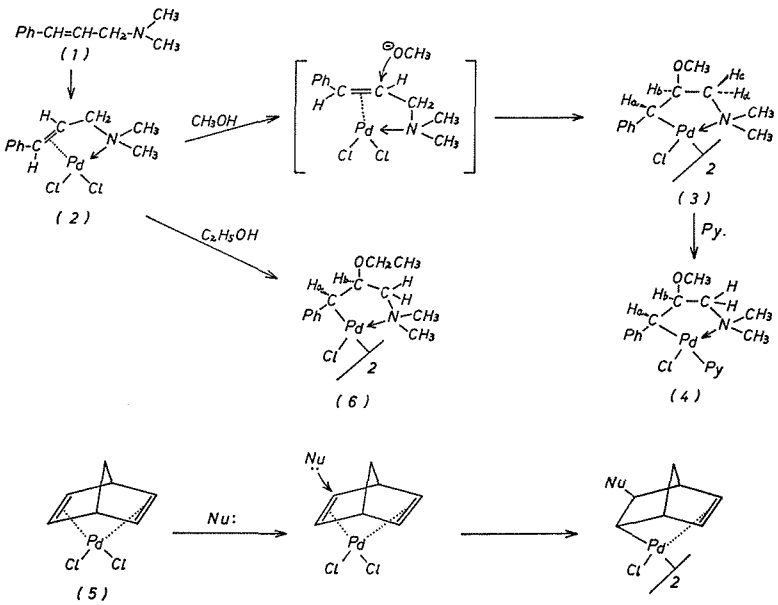

Fig. I

Experimental

Measurements and Materials. All the melting points are uncorrected. The infrared spectra were measured with a Hitachi 215 spectrometer (4000—650cm^{-1}) on KBr disks and with a Hitachi EPI-L spectrometer (700—200cm^{-1}) in nujol mulls mounted on thin polythene windows. The NMR spectra were observed by means of a Hitachi R-22 NMR spectrometer at 90MHz in $CDCl_3$ as a solvent, using TMS as an internal standard. The molecular weight was determined in benzene or in chloroform, using a Hitachi 115 molecular weight apparatus.

N,N-Dimethylcinnamylamine (**1**) was prepared according to the method described by Mitsch and Cromwell.[19] Lithium chloride and palladium chloride were of a commercial grade.

Dichloro-(N,N-dimethylcinnamylamine)-palladium(II) (**2**).

Lithium chloropalladite solutions were prepared by stirring 0.84g (20mmol) of lithium chloride and 1.77g (10mmol) of palladium chloride overnight at room temperature in 50 ml of methanol. To the lithium chloropalladite solution, **1** (1.61g, 10mmol) was added at −20°C. After 12 hr, the yellow colred precipitate was filtered off and the crude product crystallied from benzene-hexane to give yellow crystals (**2**) (2.84g, 84%). Mp 98—100°C (dec.). IR spectrum: 1422 (co-ordinated C=C), 735, 690, and 350 cm^{-1} (terminal Pd-Cl). NMR spectrum: σ 2.55 (6H, *s*, N−C**H**$_3$), 3.38 (2H, *d*, *J*=6 Hz, −C**H**$_2$−), 6.63

(1H, *d*, J=16 Hz, olefinic proton H_a), 6.98 (1H, *t—d*, J=6 and 16 Hz, olefinic proton H_b), and 7.25 *ppm* (5H, *m*, phenyl protons).
Found: C, 47.48; H, 4.25; N, 4.40%; mol wt (in berzene) 334. Calcd for $C_{11}H_{15}Cl_2NPd$: C, 47.63; H, 4.43; N, 4.11%; mol wt, 338.

Di-μ-chloro-bis-(1-phenyl-2-methoxy-3-N,N-dimethylamino-propyl)-dipalladium(II) (**3**). *a) From the reaction of* **2** *with methanol.* A suspension of **2** (1.69g, 5 mmol) in methanol (30 ml) allowed to stir at room temperature for 10 hr. The crystals of **2** dissolved to give a clear yellow solution. The solvent was then removed under reduced pressure at room temperature. The residue was recrystallized from chloroform-hexane to afford yellow crystals of **3** (1.53g, 88%). Mp 164—166°C (dec.). IR spectrum: 1100 ($-OCH_3$ stretching), 310 and 260cm^{-1} (bridged Pd—Cl). NMR spectrum: σ 3.07 (3H, *s* $-OCH_3$), 2.60(3H, *s*, $N-CH_3$), 2.78(3H, *s*, $N-CH_3$), 2.69(2H, *d—d*, $-CH_2-N$), 3.66 (1H, *d*, J=8 Hz, H_a), and 3.89 *ppm* (1H, *m*, H_b).
Found: C, 43.21; H, 5.58; N, 4.23%; mol wt (in benzene), 658. Calcd for $C_{24}H_{36}Cl_2H_2O_2Pd_2$: C, 43.10; H, 5.42; N, 4.19%; mol wt, 668.

b) From the reaction of **1** *with methanol.* To a solution containing 10 mmol of lithium chloropalladite in 70 ml of methanol, a solution of **1** (1.61g, 10mmol) in 20 ml of methanol was added. After stirring at room temperature for 10 hr, the reaction mixture was evaporated *in vacuo* to dryness and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina using dichloromethane. Recrystallization from chloroform-hexane afforded yellow crystals 3 in 64% yield. Mp 164—166°C (dec.). The IR and NMR spectra were identical with those of the complex prepared from σ-complex **2**.

(1-Phenyl-2-methoxy-3-N,N-dimethylaminopropyl)-palladium chloride pyridine (**4**). A solution of **3** (0.10g) in dichloromethane was treated with a solution of pyridine (5% excess) in ether. After stirring at room temperature for 1 hr, the solvent was removed under reduced pressure; the residue was then recrystallized from benzene-cyclohexane to give pale yellow crystals (**4**). Mp 145—149°C(dec.). IR spectrum: 1100($-OCH_3$), 740, 690, and 350cm^{-1} (terminal Pd—Cl stretching). NMR spectrum: σ 2.87(3H, *s*, $N-CH_3$), 2.97(3H, *s*, $N-CH_3$), 2.89 (2H, *d—d*, $N-CH_2-$), 3.09(3H, *s*, $-OCH_3$), 3.38(1H, *d*, J=9 Hz, H_a), 4.15(1H, *m*, H_b), and 6.82—8.81 *ppm* (10H, *m*, phenyl and pyridine protons).
Found: C, 48.08; H, 5.25; N, 6.47%; mol wt (in benzene), 417. Calcd for $C_{17}H_{23}ClN_2OPd$: C, 48.24; H, 5.47; N, 6.61%; mol wt, 423.

Di-μ-chloro-bis(1-phenyl-2-ethoxy-3-N,N-dimethylamino-propyl)-palladium (**6**).

A suspension of **2** (1.69g) in ethanol (50 ml) allowed to stir at room temperature for 19 hr. The reaction mixture was evaporated *in vacuo* to dryness and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina using chloroform. Recrystallization from benzene afforded yellow crystals(**6**), mp 135—139°C(dec.), in 65% yield. IR spectrum: 1095(O—C stretching), 758, 695, 310 and 260cm^{-1} (bridged Pd—Cl stretching). NMR spectrum: σ 0.87 (3H, *t*, $-OCH_2C\mathbf{H}_3$), 2.64 (3H, *s*, $N-C\mathbf{H}_3$), 2.76 (3H, s, $N-C\mathbf{H}_3$), 2.69 (2H, *m*, $N-C\mathbf{H}_2-$), 3.15 (2H, *q*, $-OC\mathbf{H}_2CH_3$), 3.60 (1H, *d*, J=8.0Hz, H_a), and 3.93 ppm(1H, *m*, H_b).
Found: C, 44.77; H, 5.71; N, 3.95%; mol wt (in chloroform) 688. Calcd for $C_{26}H_{40}Cl_2N_2O_2Pd_2$: C, 44.84; H, 5.79; N, 4.02%; mol wt 696.

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N,N-ジメチルシンナミルアミンのパラジウム(Ⅱ)錯体

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メタノール中，−20°Cで塩化パラジウム酸リチウムをN,N-ジメチルシンナミルアミンと反応させると，π-錯体であるジクロロー（N,N-ジメチルシンナミルアミン）—パラジウム（Ⅱ）を84%の収率で得た。室温中でこのπ-錯体をメタノールと反応させるとσ-錯体であるジ-μ-クロロービス—（1-フェニル-2-メトオキシ-3-N,N-ジメチルアミノプロピル）—ジパラジウム（Ⅱ）に変化した。このσ-錯体のNMRスペクトルよりメトオキシアニオンはπ-錯体の二重結合に対しトランス付加で反応が進行していることがわかった。